

USE OF MODEL COMPOUNDS IN COAL STRUCTURE AND REACTIVITY STUDIES

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INTRODUCTION

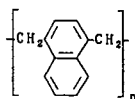
The interpretation of data from chemical and thermal reactions of coals is often facilitated and can be strengthened by investigating analogous reactions in appropriate model systems. While coal models have ranged from small molecules to polymers to synthetically coalified biomolecules and biomacromolecules, it appears that there are dangers in extrapolating the behavior of small, soluble molecules to that of solid coal. We have found that polymers and synthetic coals are much more appropriate models for coal behavior. In the present report, pyrolysis data from the latter models and coals will be compared and contrasted.

EXPERIMENTAL

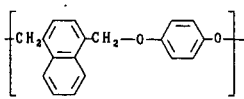
The compositions of the Argonne Premium coals and polymers used in this study are given in Table 1. The preparations of the coal samples¹ and of the two polymers² have been described.

TABLE 1. Elemental Analyses for the Argonne Premium Coal Samples.

Sample	Name	%C(maf)	Per 100 Carbons			
			H	N	S	O
8	Beulah-Zap Lignite	72.9	80	1.4	0.4	20.9
2	Wyodak-Anderson SubB	75.0	86	1.3	0.2	18.0
3	Illinois Herrin hvCB	77.7	77	1.5	1.2	13.0
6	Blind Canyon hvBB	80.7	86	1.7	0.2	10.8
7	Lewiston-Stockton hvAB	82.6	76	1.6	0.3	8.9
4	Pittsburgh hvAB	83.2	77	1.7	0.4	8.0
1	Upper Freeport mvB	85.5	66	1.5	0.3	6.6
5	Pocahontas lvB	91.0	59	1.3	0.2	2.0
	Polymer I	92.6	87	-	-	-
	Polymer II	79.6	84	-	-	11.0



I



II

Scheme 1.

GCMS and PYMS data were obtained on a Kratos MS-25 mass spectrometer. A 60 m x 0.25 mm DB-1701 fused silica column was used in GCMS analysis. The details of the PyMS experiment have been reported.³ The samples were all heated at 50°/min or at 75°/min on a platinum screen and the instrument was operated in the precise mass measurement mode.

For the very high resolution experiments, the samples were inserted into an all glass heated inlet system (300° C) and leaked into the source of a Kratos MS-50 ultra high resolution mass spectrometer.⁴ A dynamic resolution of 80,000 was obtained for the low voltage (11 eV) electron impact LVHRMS experiment with a scan rate of 1000 seconds/decade. The 70 eV EI spectra were obtained with 50,000 dynamic resolution with a scan rate of 100 seconds/decade. Both spectrometers were operated with a Kratos DS 90 data system. Data was transferred to a Micro Vax II for final analysis. The data are sorted by both heteroatom content and by hydrogen deficiency (HD). The term HD corresponds to number of rings plus number of unsaturations ($HD = -2Z$).

Synthetic Polymer Models

In the present investigation, we have examined the PyMS behavior of two synthetic polymers containing linkages presumed to exist in coals, an ethylene-linked naphthalene (I) and a hydroquinone-linked naphthalene (II). Our initial studies on the PyMS, oxidation, and liquefaction behavior of these polymers have been reported.² Solomon and coworkers have examined the pyrolysis products of similar polymers using FIMS.⁵ The PyMS techniques used in the present study have the distinct advantage of detecting and analyzing the pyrolysis products in the time-resolved mode, i.e. as soon as they are released to the vapor phase. From Figure 1, it is clear that polymer I is much less reactive than II. The pyrograms of I look much like those produced in the PyMS of inertinite macerals, with no major peak until the temperature reaches approximately 540°C. In contrast, the major devolatilization of polymer II occurs at a much lower temperature (310°C).

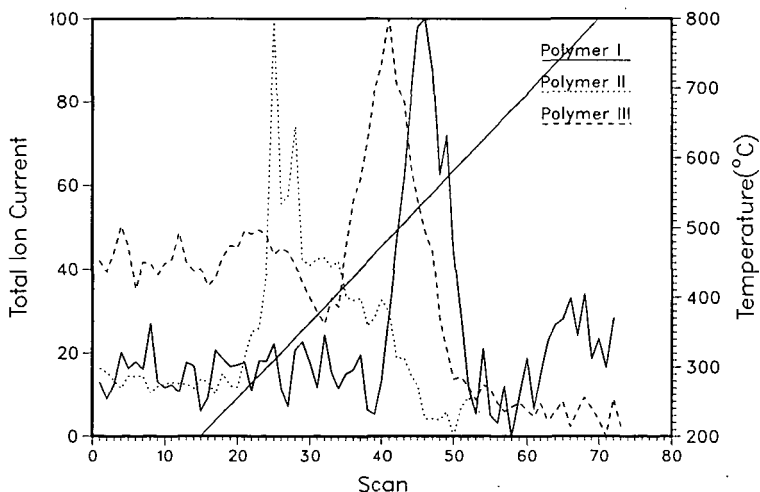
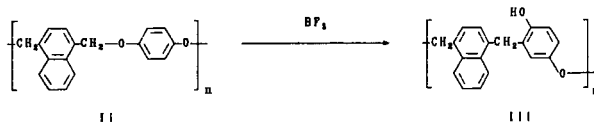


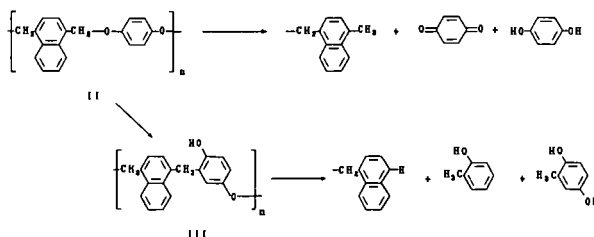
Figure 1. Total ion current pyrograms of the synthetic polymers heated beginning with scan 15 at 75° C/min from 200° to 800° in high resolution mode.

We have previously reported that attempts to unlink polymer II under mild acid conditions afforded only trace amounts of solubilized oligomeric product and almost quantitative rearrangement to a methylene linked polymer (III) as shown in Scheme 2.⁵ Both chemically and pyrolytically, the rearranged polymer, III, is much less reactive than the original oxymethylene-linked polymer, II. Pyrolysis of the rearranged polymer affords a major devolatilization peak at 480°C, 170°C higher than that of the original (Figure 1).



Scheme 2.

In addition, we have found the following convincing evidence that pyrolysis of the unrearranged oxymethylene-linked polymer II involves, as one of the reaction pathways, an analogous rearrangement to a methylene-linked polymer. In the PyMS of polymer II, a fragment with $M/Z=108$ can be due to quinone, a cresol, or a hydrocarbon. High resolution mass spectrometry makes it possible to differentiate among these species; and the results of using this technique in our PyMS experiments with polymer II are shown in Figure 2. At temperatures below 300°C, quinone but no cresols is detected while above 350°C, the reverse is observed. A very simple and reasonable explanation of these results is shown in Scheme 3.



Scheme 3.

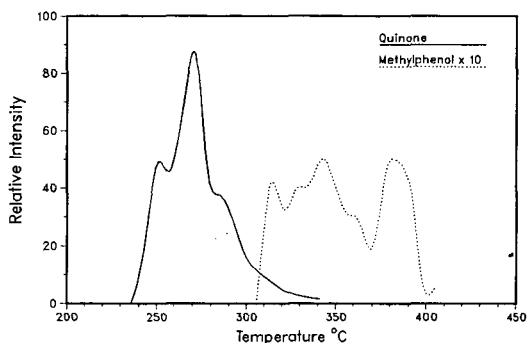


Figure 2. Selected ion chromatogram for quinone and methylphenol fragments from PyMS of Polymer II.

The time resolved high resolution MS data makes it possible to differentiate between these two different pyrolysis products even though they have the same nominal mass.

In light of these results from the model polymer, the data from PyMS of some of the Argonne Premium Coal Samples were examined for alkylated phenols and quinones. For the subbituminous coal (APCS #2) peaks which could be assigned quinone structures were observed at the lower temperatures. In Figure 3, the evolution of selected peaks are shown as a function of temperature. There is no evidence for quinones at the higher temperatures while alkylphenols are still observed. Higher rank coals such as the Illinois No. 6 (APCS #3) yielded only trace amounts of peaks corresponding to quinones while none were observed for coals with greater than 80% carbon, however, alkylphenols are observed.

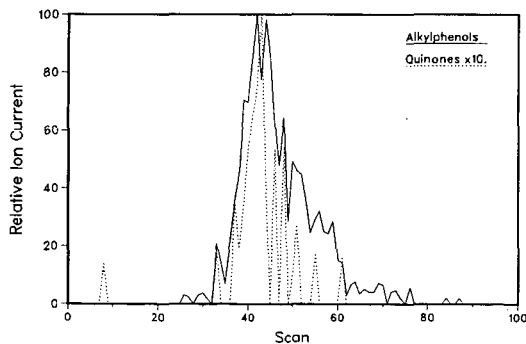
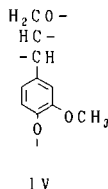


Figure 3. Selected ion pyrograms for the subbituminous coal (APCS #2).

Synthetic Coal Models

Lignins are thought to be the major precursors of vitrinite macerals. Synthetic vitrinites have been prepared heating the lignin with promotion by clays.⁷ Softwood lignins are made up mostly from the coniferyl alcohol monomers (IV). Some of the initial reactions are the loss of methyl and methoxyl with re-alkylation of the benzene ring. Also, studies of sediments confirm that these types of transformations occur.⁸



Model compounds of the softwood lignin structure were reacted under simulated coalification conditions in order to elucidate the clay-organic reactions responsible for bond cleavage and rearrangement processes in these systems. Of specific interest was the reactivity of anisole (phenyl methyl ether) groups in these model compounds, which include *m*-methyl anisole (mMA), guaiacol, 4-hydroxy-3-methoxy toluene and 4-phenoxy-3-methoxy toluene. Pillared clays (PILCs) were chosen as the catalysts because they are an order of magnitude more active than untreated clays under these specific conditions. PILCs are smectite clays with permanent intracrystalline porosity made by metal oxide molecular props, usually alumina, that hold the clay layers apart.

The predominant reaction observed is O-methyl bond cleavage of anisoles to lead to phenolic functionality. Transalkylation and dealkylation reactions are also observed by GCMS and solid-state ¹³C NMR techniques. In addition, isotopically labeled ¹³C anisoles were synthesized and reacted with clays. Mass spectra of volatile products reveal the presence of ¹³CH₃OH and large amounts of (¹³CH₂)₂O due to further dehydration of methanol over the clay surface.

Table 2 gives the distribution of solvent-extractable products obtained from mMA catalysis as determined by GCMS. The amount of mMA decreases as it is reacted to *m*-cresol and alkylated cresols (major products), and alkylated anisoles (minor products). The amount of dialkylated products begins to decline after a certain amount of reaction time, as they are further cracked to simpler products.

TABLE 2. Distribution (mole %) of soluble products obtained from the reaction of *m*-methyl anisole with pillared bentonite clay at 150° C.

Product	Time (hours)			
	0	22	49	72
mMA	100	69.2	9.4	4.9
Me-mMA	0	3.3	9.8	10.1
Me ₂ -mMA	0	0	1.8	1.0
<i>m</i> -cresol	0	27.7	33.2	34.8
Me-cresol	0	0	24.5	41.4
Me ₂ -cresol	0	0	21.3	7.8

mMA = *m*-methyl anisole

Me = methyl

These results give an indication of the types of reactions that occur under simulated coalification conditions. These necessarily involve heterogeneous interactions with a solid acid catalyst and reactions that are typically catalyzed by protons.

From the model studies one would predict that the number of benzene rings with two oxygen substituents would decrease with increasing rank. Also, the overall phenolic content should decrease with rank. PyHRMS data have been obtained for the eight Premium Coal Samples. An estimate of yields of phenols from the high vacuum pyrolysis is shown in Figure 4. The trends observed are as expected except for the Utah Blind Canyon Coal (APCS #6). This coal is rich in liptinites which would mean that the products would be dominated by the high yield hydrocarbons from the liptinites. Overall, the species with two oxygens decrease rapidly after about 78% carbon content. The Illinois No. 6 coal may be a little unusual since it has a fairly high oxygen content for a high volatile bituminous coal. There appears to be a significant amount of lignin character left in the lignite. This conclusion is supported by oxidative degradation data and by characterization of extracts from lignite.

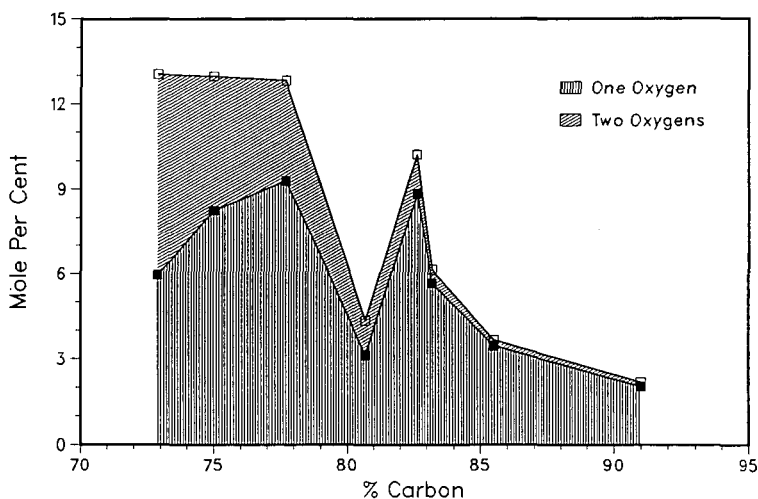


Figure 4. Phenols from PyHRMS of the Premium Coals presented as a stacked plot.

CONCLUSIONS

It would be very difficult to say anything about chemical structures in coals without results from model systems. Many times the systems were not studied as a model for coals, but the results can still be used to interpret the coal data when similar methods are used. Macromolecular models can be quite realistic and some of the examples described in this paper show how they can be used to better understand the coal results. However, one must be careful that the model results are not over-interpreted much like the problem that has occurred with drawing or modeling of "average structures."

ACKNOWLEDGMENTS

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